Mineral surface controls on Cr(VI) reduction by sorbed Fe(II)

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For redox-sensitive contaminants such as chromium, the kinetics of different reduction pathways can vary by orders of magnitude. Species-specific rate constants for iron-chromium oxidation-reduction reactions are unknown for many systems, especially in the presence of sorbing surfaces. The presence of mineral surfaces has been shown to increase the rate of hexavalent chromium (Cr(VI)) reduction by ferrous iron (Fe(II)), but this effect has been ascribed to multiple physiochemical processes.

Our prior study of sorption edges, surface complexation modeling, and EXAFS spectroscopy of Zn(II) sorbed to variably nanoporous and crystalline silica showed that nanopores and surface disorder alter Zn-O coordination of surface complexes. If similar coordination changes occur for Fe(II) sorbed to silica surfaces, the rate of Cr(VI) reduction could be altered. Batch sorption and redox experiments involving the Cr(VI)-Fe(II)-quartz and Cr(VI)-Fe(II)-$SiO_{2(am)}$ systems illustrate the role of silica surfaces in mediating abiotic reduction of Cr(VI) by aqueous and sorbed Fe(II) species. Sorption edges indicate that outer-sphere ($Fe(II)_{ads,OS}$) and inner-sphere ($Fe(II)_{ads,IS}$) complexes are present on both silica substrates, but their abundance depends on pH, ionic strength, and surface disorder. The rate constants for $Cr(VI)_{aq}$ reduction by Fe(II) species increase in the following order: $k_{aq} << k_{ads,OS,quartz} < k_{ads,OS,SiO2(am)} < k_{ads,IS,quartz} < k_{ads,IS,SiO2(am)}$. No effect of nanoporosity was observed. As the reaction proceeds and Cr(III)-Fe(III) precipitates form on the silica surface, a portion of the sorbed Fe(II) is sequestered ($Fe(II)_s$) into the precipitate. Therefore, the balance between increases in the rate and decreases in the total amount of $Cr(VI)_{aq}$ reduction by various sorbed Fe(II) species must be considered when devising remediation strategies in Fe(II)-limited systems.